First order reversal curve analysis of nanocrystalline Pd$_{80}$Co$_{20}$ alloy films

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ABSTRACT

Films of isotropic nanocrystalline Pd$_{80}$Co$_{20}$ alloys were obtained by electrodeposition onto brass substrate in plating baths maintained at different pH values. Increasing the pH of the plating bath led to an increase in mean grain size without inducing significant changes in the composition of the alloy. The magnetocrystalline anisotropy constant was estimated and the value was of the same order of magnitude as that reported for samples with perpendicular magnetic anisotropy. First order reversal curve (FORC) analysis revealed the presence of an important component of reversible magnetization. Also, FORC diagrams obtained at different sweep rate of the applied magnetic field, revealed that this reversible component is strongly affected by kinetic effect. The slight bias observed in the irreversible part of the FORC distribution suggested the dominance of magnetizing intergrain exchange coupling over demagnetizing dipolar interactions and microstructural disorder.

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1. Introduction

A variety of techniques have been used over the last decades for the production of PdCo and PtCo alloy films including evaporation, DC magnetron sputtering, molecular beam epitaxy, electrodeposition and e-beam evaporation [1–6]. Research efforts have, however, focused mainly on the magnetic properties of Co/Pd multilayer films because of their potential use in high-density perpendicular magnetic recording media [7–12]. However, PdCo alloy films exhibit excellent mechanical properties such as high levels of hardness and corrosion resistance and, consequently, durability. Additionally, PdCo alloys are of interest by virtue of their important applications in heterogeneous catalysis and corrosion processes [13].

Electrodeposition represents a fast and relatively cheap method for growing high-quality thin films on diverse substrates, and offers a number of advantages in comparison with vacuum deposition techniques. Films grown by electrodeposition are easily reproducible when the optimal values for the growth parameters have been determined. Moreover, electrodeposits of PdCo are usually formed with high internal stresses, thus increasing the magnetostriction and the effective magnetocrystalline anisotropy and, consequently, the coercivity of the alloy. Accordingly, these materials currently appear to be very promising candidates for use in magnetic random access memory (MRAM) and ferroelec-

tric random access memory (FRAM) [6], and also as permanent nanomagnets in, for example, microelectromechanical systems (MEMS).

Coercivity is strongly influenced by the microstructure of the electrodeposits and by the production process. It has been recently demonstrated that the mean grain size of electrodeposits of PdCo alloy films may be controlled, without substantial changes in alloy composition, by variation of the pH of the electrodeposition bath [14]. Effectively, isotropic nanostructured films of composition Pd$_{80}$Co$_{20}$ and mean grain sizes in the range 18–23 nm were obtained by galvanostatic electrodeposition from a chloride plating bath of pH between 5.5 and 8.5. Moreover, the electrodeposits showed lattice strain percentages and mean crystallite sizes that were related to the pH of the bath. Even though the magnetic properties of the films were entirely isotropic, the enhancement of the coercive field H_c was noticeable and displayed a maximum value of 1.7 kOe for the sample with the smallest grain size.

The analysis of first order reversal curve (FORC) diagrams represents a phenomenological approach that has received much recent interest for investigating hysteresis in magnetic systems [15–17]. A FORC distribution provides a detailed characterization of the hysteretic response of a magnetic system to an applied field by revealing the dominant interactions in the system, the magnetic viscosity effects and the destruction of memory during a demagnetization process. The objective of the present study was to carry out a detailed investigation of the interparticle magnetic interactions and the magnetization reversal process in Pd$_{80}$Co$_{20}$ alloy films.

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Table 1
Physical properties of $Pd_{80}Co_{20}$ films electrodeposited in plating baths with different pH values.

Plating bath pH	Lattice constant a (nm)	Composition of film[a]	Mean grain size (nm)	Lattice Strain (%)	Curie temperature T_C (K)	Coercivity H_c (kOe)	Squareness[b] m_R/m_S
5.5	0.383(1)	$Pd_{80}Co_{20}$	18.2 ± 1.0	0.63(1)	639(3)	1.69(2)	0.57
6.5	0.385(1)	$Pd_{80}Co_{20}$	19.4 ± 1.0	0.58(1)	642(3)	1.63(2)	0.55
7.5	0.384(1)	$Pd_{79}Co_{21}$	21.0 ± 1.0	0.53(1)	634(3)	1.52(2)	0.53
8.5	0.384(1)	$Pd_{79}Co_{21}$	22.8 ± 1.0	0.48(1)	637(3)	1.37(2)	0.51

[a] Results derived from energy dispersive X-ray spectrometry (with ±2% atomic deviation).

[b] m_R: remanent magnetization and m_S: saturation magnetization.

2. Experimental procedure

The PdCo alloy films studied were produced by electrodeposition in the galvanostatic mode onto commercial grade brass substrate using a previously described method [14]. A Kraft Dynatronix (Amery, WI, USA) model DPR 20-5-10 power source was employed to provide a constant current equal to 1 A, and films with enhanced magnetic characteristics, including coercivity and saturation magnetization [18], were prepared with an electrical current density of 250 mA/cm^2 and an electrical charge of 100 C for each deposit. The alloy composition of each film was estimated by energy dispersive X-ray spectrometry (EDS), and the thickness and current efficiency were determined from the mass of the deposit and its composition.

The physical characteristics of the deposits were assessed by scanning electron microscopy (SEM) and X-ray diffractometry (XRD). In the XRD experiments, CuKα (1.54 Å) radiation was produced at 40 kV and 30 mA using a Siemens D 5000 X-ray generator with a monochromator in the diffracted beam. Measurements in the range 20–70° with a step size of 0.05° and a step time of 15 s were recorded in order to obtain the general pattern. The average crystallite size was determined according to Scherrer's formula [19] using a slower scanning speed in order to prevent peak enlargement, and the range recorded was 35–55° with a step size of 0.01° and a step time of 15 s. Lattice strain associated with the residual stress originating from the electrodeposition process was also estimated from the XRD patterns [20,21].

Hysteresis loops at room temperature were determined by measuring the magnetic moment as a function of magnetic field using an EG & G PAR (Ametek, Oak Ridge, TN, USA) model 4500 vibrating sample magnetometer coupled to a 90-kOe superconducting coil (Janis Research Company, Wilmington, MA, USA). A set of FORC were obtained by: (i) saturating the sample by applying a field H_{max} (in the present case H_{max} = 30 kOe), (ii) setting the field H to a return value H_r where $H_r < H_{max}$, (iii) increasing H back to H_{max} and measuring the magnetization, and (iv) repeating steps (ii) and (iii) for decreasing values of H_r where $H_r \geq -H_{max}$. The FORC distribution may then be defined in terms of the magnetization function $M(H_r, H)$ by the mixed derivative:

$$\rho(H_r, H) \equiv -\frac{1}{2}\frac{\partial^2 M(H_r, H)}{\partial H_r \partial H} \tag{1}$$

which is plotted in a 45°-rotated system of coordinates $\{h_c, h_b\}$ given by $\left\{ h_c = \frac{1}{2}(H - H_r), \quad h_b = \frac{1}{2}(H + H_r) \right\}$.

3. Results and discussion

The main physical properties of the PdCo alloy films studied in the present work are summarized in Table 1. Previously published SEM micrographs of our PdCo films obtained with plating baths at pH values of 5.5 and 6.5 displayed crystallites with dendritic morphology and arranged on the substrate plane with random orientation [14]. However, when the pH of the plating bath was increased to 7.5 or 8.5, the morphology of the crystallites changed to reveal cauliflower-like shapes.

The XRD patterns of the PdCo alloy electrodeposits are shown in Fig. 1 in which two peaks (labeled BS) are associated with the brass substrate while three peaks are characteristic of the face-centered cubic (fcc) structure of Pd. No peaks in the XRD patterns could be attributed to Co indicating that this metal was, as expected, dissolved in the Pd matrix to form a substitutional solid solution with an fcc structure, a result that is agreement with the phase diagram of the PdCo alloy [22]. Small quantities (<3%) of pure Pd or Co may have been present in the alloy, but no evidence for the presence or absence of such components were obtained in the present study.

The lattice constants of each of the films studied are displayed in Table 1. The results obtained by energy dispersive spectrometry correspond approximately to an alloy composition of $Pd_{80}Co_{20}$ with an atomic deviation of ±2%, and this value is in full accord
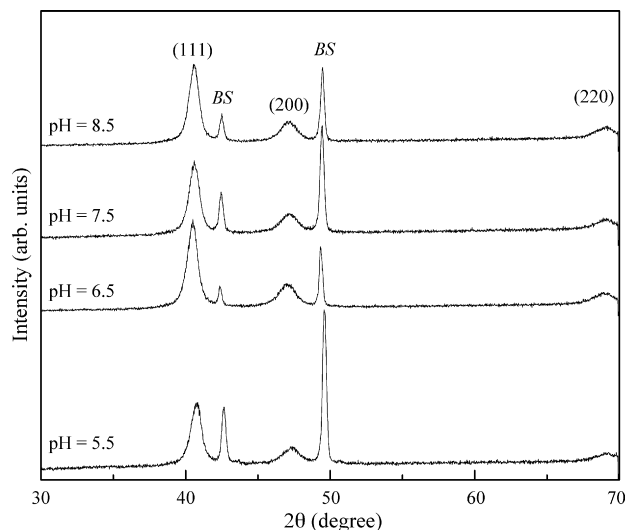

Fig. 1. X-ray diffraction patterns of $Pd_{80}Co_{20}$ alloy films prepared by electrodeposition in a pH controlled plating bath.

with the lattice constant obtained from the positions of the X-ray diffraction lines (cf. Table 1 in Shi et al. [23]). The mean grain sizes, derived from the XRD patterns by application of Scherrer's formula [19], were proportional to the pH of the plating bath (Fig. 2). The lattice strain percentages shown in Table 1 were also calculated from the corresponding XRD patterns as described previously [20,21], and revealed an inverse proportionality with the pH of the plating bath. The coefficient of thermal expansion of the brass substrate ($\alpha_{brass} \approx 20 \times 10^{-6}$ K^{-1}) was close to that of the PdCo film
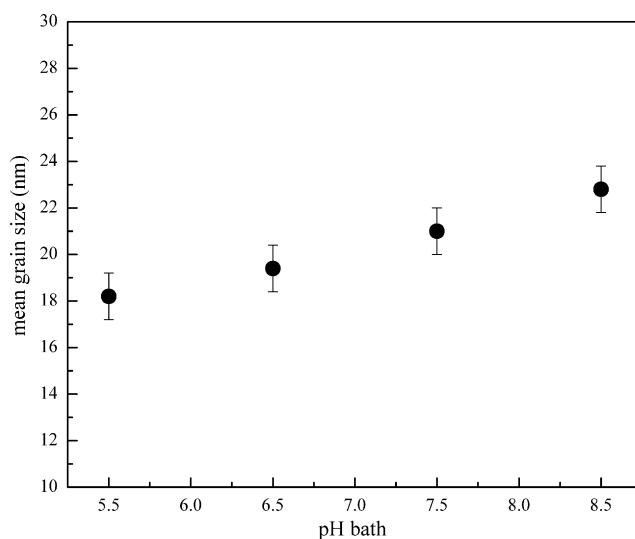

Fig. 2. Relation between the mean grain size of $Pd_{80}Co_{20}$ alloy films and the pH of the plating bath employed in the electrodeposition procedure.